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Testing the time-invariance of fundamental constants using microwave spectroscopy on cold diatomic radicals

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The recently demonstrated methods to cool and manipulate neutral molecules offer new possibilities for precision tests of fundamental physics theories. We here discuss the possibility of testing the time-invariance of fundamental constants using near degeneracies between rotational levels in the fine structure ladders of molecular radicals. We show that such a degeneracy occurs between the $J = 6$, $\Omega = 1$ and the $J = 8$, $\Omega = 0$ levels of the various natural isotopomers of carbon monoxide in its $a^3\Pi$ state. As a result, the 2-photon transition that connects these states is 300 times more sensitive to a variation of m_p/m_e than a pure rotational transition. We present a molecular beam apparatus that might be used to measure these transitions with a fractional accuracy of 10^{-12}. Ultimately, the precision of an experiment on metastable CO will be limited by the lifetime of the $a^3\Pi$ state. We will discuss other possible molecules that have a suitable level structure and can be cooled using one of the existing methods.

Introduction

The equivalence principle of general relativity postulates that the outcome of any non-gravitational experiment is independent of position and time. In theories that attempt to unify gravity with other fundamental forces, on the other hand, violation of the equivalence principle may occur and can be consistently described. The Kaluza–Klein theories from the 1920s as well as modern string theories, for instance, introduce additional compactified dimensions, and the size of these—yet unobserved— dimensions determines the strength of the fundamental forces. If the size of these dimensions should happen to change over time, the strength of the forces in four-dimensional space–time would change as well. Such a change would manifest itself as a change of the coupling constants and particle masses.[1]

From an experimental perspective, it is most practical to search for variation of dimensionless quantities. The fine structure constant, α, representing the strength of the electro-weak force, and the proton–electron mass ratio, $\mu = m_p/m_e$, which is a measure for the strength of the strong force, are the prime targets of modern research in this area. Possible variations can be detected from a wide variety of physical phenomena, but the extreme accuracy that can be obtained in the determination of frequencies or wavelengths of spectral lines in atoms and molecules makes spectroscopy the ideal testing ground for searches of varying α and μ.[2] The proton–electron mass ratio is of particular interest as theoretical models predict that the variation of μ could be significantly larger than the variation of α. Calmet and

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Fritsch, for instance, predict that the variation of μ is 38 times larger than the variation of α.[3]

Recent astrophysical data suggest that the fine structure constant, α, has increased over cosmological time. The combined analysis over more than 100 quasar systems has produced a value of a relative change of $\Delta\alpha/\alpha = -0.57 \pm 0.10 \times 10^{-5}$, which is at the 5σ significance level.[4] Based on the spectral lines of molecular hydrogen in two quasar systems at redshifts of $z = 2.6$ and $z = 3$, an indication was found of a relative decrease of the proton–electron mass ratio, μ, of two parts in 10^5 over cosmological time.[5] If one assumes that the constants change linearly over time, this implies a fractional change on the order of 10^{-15} per year. To test the time-variation of fundamental constants in the current epoch, frequency standards based on different atomic and molecular transitions are being compared as a function of time. As these standards have in general a different dependence on α and μ, a possible time-variation of α and/or μ will lead to a frequency shift. In contrast to astrophysical observations, which measure the constants' value over a significant fraction of the age of the universe, laboratory tests cover only a short time span. Their advantage, however, is their great accuracy, reproducibility and unequivocal interpretation.

Currently, laboratory experiments have found no indications for the time-variation of any fundamental constant. The most stringent limit is set by a comparison between an optical mercury ion clock and a caesium fountain clock over 6 years. Assuming invariance of other constants, this results in a limit for the variation of $\Delta\alpha/\alpha < 1.3 \times 10^{-16}\ \mathrm{yr}^{-1}$.[6] The most stringent *independent* test of the time-variation of μ is set by comparing vibrational transitions in SF_6 with a caesium fountain over 2 years, which has resulted in a limit for the variation of $\Delta\mu/\mu < 5.6 \times 10^{-14}\ \mathrm{yr}^{-1}$.[7]

The sensitivity of any experiment looking for a frequency shift, $\Delta\nu$, due to the time-variation of a fundamental constant, X, depends both on the size of the shift, *i.e.*, the inherent sensitivity of the atomic or molecular transition, and on the ability to measure this shift. As a measure for the inherent sensitivity of a transition, we introduce a sensitivity coefficient, K, *via*:

$$\frac{\Delta\nu}{\nu} = K_X \frac{\Delta X}{X}$$

Generally, two strategies can be followed: (i) one uses a system that is naturally suitable for precision measurements—*i.e.*, a system that can be well controlled by *e.g.*, laser cooling techniques, offers a high Q-factor, a high signal to noise, *etc.*—but has typically a sensitivity on the order of unity. (ii) one uses a system that has a large sensitivity, but that is not necessarily ideal for precision measurements. At present, most currently running and proposed[8] experiments take the first approach. A notable exception is the experiment of Cingöz *et al.* on atomic dysprosium.[9]

Atomic dysprosium has a unique property of an accidental near degeneracy between two high lying energy levels that have a different symmetry and move in opposite directions if α varies. As a result, the rf transition between the two levels has a fractional sensitivity to a variation in α of about 10^6. Note that, given a certain change of α, the resulting absolute frequency shift of the energy levels in dysprosium is comparable to that in, for instance, the mercury ion. However, whereas in the mercury ion this shift needs to be measured on an optical frequency, in dysprosium this shift can be measured on an rf frequency. The latter is usually much simpler. For example, the fractional frequency uncertainty of the current best optical standard—the mercury ion clock—is on the order of 10^{-17}, which corresponds to an absolute frequency uncertainty of 10 mHz.[6] The current best microwave standard—the caesium fountain clock—has a fractional frequency uncertainty of 10^{-16}, which corresponds to an absolute frequency uncertainty of 1 μHz.[10]

Whereas in atoms a near degeneracy between levels of different symmetry is very rare, in molecules this happens rather frequently. DeMille *et al.*[11] proposed a test

based on a near degeneracy between the $a^3\Sigma_u^+(v = 37)$ and the $X^1\Sigma_g^+(v = 138)$ in Cs_2. Flambaum[12] proposed to use diatomic molecules with unpaired electrons, such as LaS, LaO, LuS, LuO, YbF and similar ions, that have a cancellation between their hyperfine and rotational interval. Kozlov and Flambaum[13] proposed to use diatomic molecules that have a cancellation between their fine structure and vibrational interval and identified Cl_2^+, CuS, IrC, SiBr and HfF^+ as suitable candidates.[14] These cancellations occur in heavy molecules which, however, do not lend themselves well to the recent developed cooling and manipulation techniques based on time-varying electric or magnetic fields.[15]

In this paper we propose another system that is suitable for detecting μ-variation in a laboratory experiment, in this case because of a near degeneracy between rotational levels in the fine structure ladders of a $^2\Pi$ or $^3\Pi$ state. Such a degeneracy is shown to occur in the various natural isotopomers of carbon monoxide in its $a^3\Pi$ state, which is metastable. We discuss the precision that might be obtained using metastable CO and discuss other (including ground-state) molecules that have a suitable level structure.

The sensitivity of molecular transitions to a variation of α or μ

In the Born–Oppenheimer approximation, the motion of the molecule is separated into an electronic and nuclear part. The physical basis of this separation is that the nuclei are much heavier than the electrons and hence move at much slower speeds. The nuclear motion can be further separated into a vibrational part and a rotational part. The energy difference between electronic states is much larger than the energy difference between vibrational states within an electronic state, and the energy difference between vibrational states is correspondingly larger than the energy difference between rotational states. We thus have a hierarchy of states which reveals itself in electronic, vibrational and rotational spectra of molecules. The energy of a closed shell diatomic molecule can be written as;

$$E_{v,J} = T_e + \omega_e(v + 1/2) + \omega_e x_e(v + 1/2)^2 + \ldots + B_e J(J + 1) - D_e J^2(J + 1)^2 + \ldots - \alpha_e(v + 1/2)J(J + 1) + \ldots$$

with T_e being the electronic energy, ω_e and $\omega_e x_e$ being the harmonic an anharmonic vibrational constant, B_e and D_e being the rotational constant and the centrifugal distortion constant, and v and J are the vibrational and rotational quantum numbers, respectively. α_e is the lowest order coupling term between the vibrational and rotational motion in the molecule.[16,17]

In order to determine the sensitivity of a certain molecular transition to a possible change of the proton to electron mass ratio, μ, we must determine the dependence of the molecular constants to μ. If we assume that the neutron to electron mass ratio changes at the same rate as the proton to electron mass ratio, we find that:

$$\frac{\Delta\mu}{\mu} = \frac{\Delta\mu_N}{\mu_N}$$

with μ_N being the reduced nuclear mass of the molecule. Thus, the dependence of the molecular constants on μ can be found by using the well known scaling relations upon isotopic substitution—the favorite method of the spectroscopist to aid the assignment of molecular spectra. The following relations hold[16]

$$T_e \propto \mu^0, \quad \omega_e \propto 1/\sqrt{\mu}, \quad \omega_e x_e \propto 1/\mu$$
$$B_e \propto 1/\mu, \quad D_e \propto 1/\mu^2, \quad \alpha_e \propto 1/\mu^{1.5}$$

Thus we see that pure electronic transitions do not depend on μ (but do depend on α). Transitions between low lying vibrational levels have $K_\mu = ½$, while K_μ is below

½ for transitions between higher vibrational levels due to anharmonicity. Transitions between low lying rotational states have $K_\mu = 1$, while K_μ is below 1 for transitions between higher lying rotational states where centrifugal distortion becomes significant. Note that in more complex molecules, additional degrees of freedom and intramolecular motions play a role which may lead to an enhancement of the sensitivity to a variation in μ. The inversion frequency in the ground state of ammonia, for instance, has a sensitivity equal to $K_\mu = 4.6$.[18,19]

Let us now turn to diatomics with open shell electronic states—so called free radicals. The interaction between the electronic orbital angular momentum, $\boldsymbol{L}$, the spin angular momentum, $\boldsymbol{S}$, and the rotational angular momentum, $\boldsymbol{R}$, give rise to additional structure as compared to a closed shell molecule. Two cases can be distinguished:[16,17] (i) Hund's case (a); $\boldsymbol{L}$ is strongly coupled to the internuclear axis and $\boldsymbol{S}$ couples to the electronic orbital angular momentum vector *via* spin-orbit interaction. (ii) Hund's case (b); the $\boldsymbol{S}$ is decoupled from the internuclear axis, the orbital angular momentum couples to $\boldsymbol{R}$ to form $\boldsymbol{N}$, which then couples to $\boldsymbol{S}$.

We will be interested in molecular states that are well described by Hund's case (a) coupling scheme for reasons that will become obvious. In Hund's case (a), molecular levels are labeled by the total angular momentum, J, by the projection of $\boldsymbol{L}$ on the internuclear axis, Λ, by the projection of $\boldsymbol{S}$ on the internuclear axis, Σ, and by the projections of $\boldsymbol{J}$ on the internuclear axis, Ω, and on the space fixed axis, M. There are $2S + 1$ fine structure levels, characterized by their Ω values. These levels have energies of $A_e\Lambda\Sigma$, with A_e being the spin–orbit constant. Each fine-structure state has a pattern of rotational levels with energies given by $B_eJ(J + 1) - D_eJ^2(J + 1)^2\ldots$, with $J = \Omega$ being the lowest level. In light molecules, A_e is comparable to B_e, whereas in heavy molecules A_e becomes comparable to ω_e. In Hund's case (a), the electronic motion can in first order be separated from the nuclear motion; that is, the energy differences between the different Ω-manifolds depend on α but not on μ. This has as interesting consequence that when two rotational levels of different Ω-manifolds have a near degeneracy, the sensitivity of a transition connecting these two levels to a variation of α and μ is enhanced by a factor A_e/ν, with ν being the frequency of the transition in energy units. As an example we will study such near degeneracies in metastable CO.

Metastable CO

The metastable $a^3\Pi$ state in CO is one of the most extensively studied triplet states of any molecule. It has been studied using rf,[20] microwave[21] and UV-spectroscopy.[22] The lifetime of the $a^3\Pi$ state depends strongly on the rotational level and ranges from 2.6 ms in the $v = 0$, $J = 1$, $\Omega = 1$ level to 140 ms in the $v = 0$, $J = 2$, $\Omega = 2$ level. Rotational levels in the $v = 0$ and $v = 1$ of the $a^3\Pi$ state can be directly excited using laser radiation around 206 and 199 nm, respectively.[23] Due to its favorable properties, metastable CO was used in the first demonstration of Stark deceleration.[24] Recently, metastable CO was trapped in an electrostatic trap and its lifetime directly measured by monitoring the trap-decay.[25]

We have calculated the excitation energy of the rotational levels of the $a^3\Pi$ state using the model of Field *et al.*[22] In this model, the wavefunctions are a superposition of pure Hund's case (a) wavefunctions.[26] The energies of the lower rotational levels are shown in Fig. 1. The component of the total electronic angular momentum along the internuclear axis Ω takes on the values $\Lambda + \Sigma = 0,1,2$, resulting in three Ω-ladders. Each J-level is split by the Λ-doubling into two components with opposite parity. The Λ-doubling in the $\Omega = 0$ state is large and relatively independent of J. The Λ-doubling in the $\Omega = 1$ state is much smaller and in the $\Omega = 2$ state even smaller still.

For pedagogic reasons, we will first examine 1-photon transitions between the different Ω-manifolds. We are looking for transitions with as small a frequency as

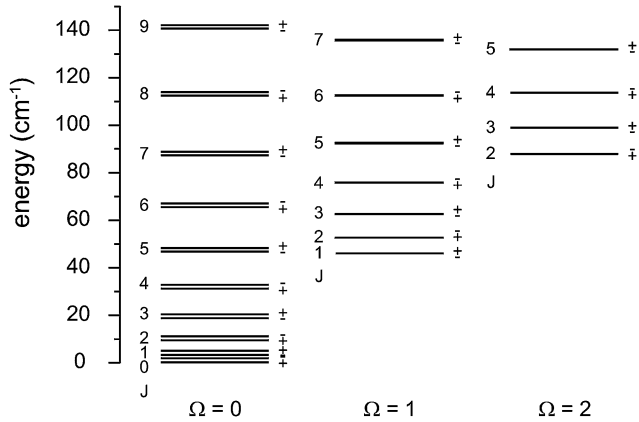

Fig. 1 Energy of the lowest rotational levels of the $a^3\Pi$ ($v = 0$) state of $^{12}C^{16}O$.

possible, hence we look at transitions $J - 1$, $\Omega = 2 \rightarrow J$, $\Omega = 1$ and J, $\Omega = 1 \rightarrow J + 1$, $\Omega = 0$. As the total parity changes sign in a 1-photon transition, transitions only connect upper Λ-doublet levels to upper Λ-doublet levels and lower Λ-doublet levels to lower Λ-doublet levels. Hence, for every J, we have a total of 4 transitions. These 4 transitions are shown in the upper panel of Fig. 2 as a function of J. Naively, we expected a minimum transition frequency to occur when $A_e \approx 2B_eJ$. For the $a^3\Pi$ state of $^{12}C^{16}O$, $A_e = 41.45\ cm^{-1}$ and $B_e = 1.68\ cm^{-1}$,[22] thus, we expected a minimum transition frequency when $J \approx 12$. From the figure, we see that although the energy difference initially becomes rapidly smaller as J increases—as is obvious from the tangent at low J shown as dashed lines—the energy difference converges to a constant. We can understand this as a transition from a Hund's case (a) to a Hund's case (b) coupling scheme. At higher J, the spin becomes uncoupled from the internuclear axis and the electronic and nuclear motion can no longer be separated. As a consequence the sensitivity to a μ-variation for transition between the different Ω-manifolds at high J is similar to pure rotational transitions.

Let us now turn to 2-photon transitions, *i.e.*, transitions from $J-2$, $\Omega = 2 \rightarrow J$, $\Omega = 1$ and J, $\Omega = 1 \rightarrow J + 2$, $\Omega = 0$. Again transitions only connect upper Λ-doublet levels to upper Λ-doublet levels and lower Λ-doublet levels to lower Λ-doublet levels because parity is conserved in a 2-photon transition. Hence, we have 4 transitions for every J. These 4 transitions are shown in the lower panel of Fig. 2 as a function of J. A minimum energy difference is now expected when $A_e \approx 4B_eJ$; *i.e.*, when $J \approx 6$, as is indeed observed.

In Fig. 3, the transitions from $J = 4$, $\Omega = 2 \rightarrow J = 6$, $\Omega = 1$ and $J = 6$, $\Omega = 1 \rightarrow J = 8$, $\Omega = 0$ are shown for the most common isotopomers of CO. Here the effects of nuclear spin and hyperfine structure have been neglected. The molecular constants are obtained *via* isotope scaling of the constants of $^{12}C^{16}O$ *via* the relations discussed earlier. The large isotope shift of the transitions is indicative of a large sensitivity to a variation of μ. The solid lines plotted in the figure, follow the relation $E = \text{constant} + \mu_N \times 72.5\ [\text{GHz amu}^{-1}]$, with μ_N being the reduced nuclear mass. From this we can determine the sensitivity, $K_\mu = 2\mu_N \times 72.5\ [\text{GHz amu}^{-1}]/\Delta E$, with ΔE being the energy difference between the two near degenerate levels. Similar calculations have been performed for the $v = 1$ state (not shown). Due to the smaller B constant in the $v = 1$, the energy differences of the different transitions are slightly larger (more positive). As a result, in the $v = 1$ state the $J = 6$, $\Omega = 1$ lies slightly above the $J = 8$, $\Omega = 0$, whereas in the $v = 0$ state the $J = 6$, $\Omega = 1$ lies slightly below the $J = 8$, $\Omega = 0$.

All transitions with frequencies below 25 GHz are listed in Table 1 together with their sensitivity to a variation of μ. Particularly interesting are the two transitions in

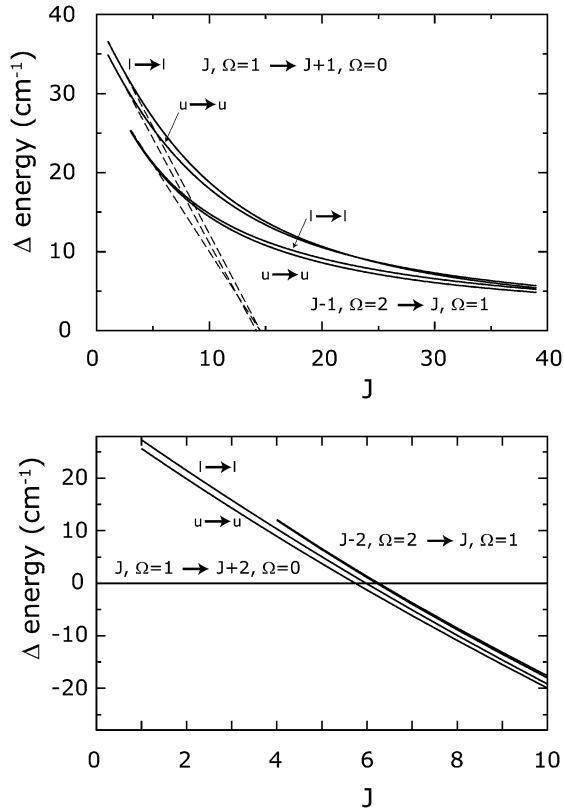

Fig. 2 Energy difference between $J-1$, $\Omega=2$ and J, $\Omega=1$ levels and between $J+1$, $\Omega=0$ and J, $\Omega=1$ levels (1-photon transitions) (upper panel) and energy difference between $J-2$, $\Omega=2$ and J, $\Omega=1$ levels and between J, $\Omega=1$ and $J+2$, $\Omega=0$ levels (2-photon transitions) (lower panel) in the $a^3\Pi$ ($v=0$) state of $^{12}C^{16}O$.

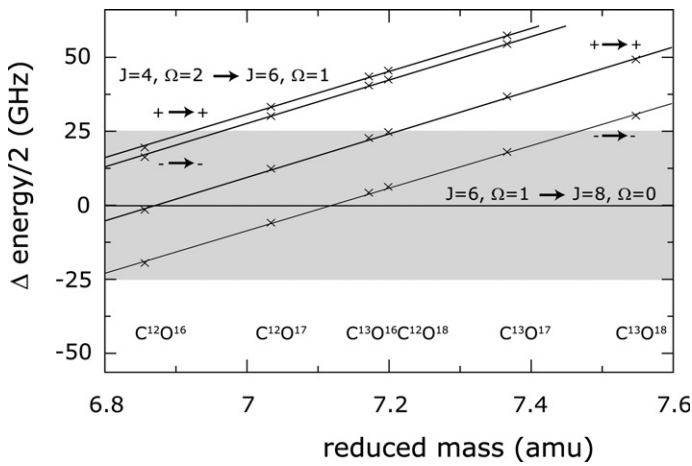

Fig. 3 Energy of selected 2-photon transitions in the $a^3\Pi$ ($v=0$) state of (different isotopomers of) CO. The sensitivity for a change of μ is apparent from the large isotope shift of the transition.

Table 1 Frequencies of selected 2-photon transitions in the $a^3\Pi$ state of (different isotopomers of) CO together with their sensitivity to a μ-variation

	ν/GHz	Isotope	Transition	Sensitivity, K_μ
1	1.648	$C^{12}O^{16}$	$v=0, J=6, \Omega=1, + \rightarrow v=0, J=8, \Omega=0, +$	−302
2	1.9	$C^{12}O^{17}$	$v=1, J=6, \Omega=1, - \rightarrow v=1, J=8, \Omega=0, -$	−264
3	2.459	$C^{12}O^{16}$	$v=1, J=6, \Omega=1, + \rightarrow v=1, J=8, \Omega=0, +$	202
4	4.1	$C^{13}O^{16}$	$v=0, J=6, \Omega=1, - \rightarrow v=0, J=8, \Omega=0, -$	126
5	6.0	$C^{12}O^{17}$	$v=0, J=6, \Omega=1, - \rightarrow v=0, J=8, \Omega=1, -$	−86
6	6.1	$C^{12}O^{18}$	$v=0, J=6, \Omega=1, - \rightarrow v=0, J=8, \Omega=0, -$	86
7	8.0	$C^{13}O^{16}$	$v=1, J=6, \Omega=1, - \rightarrow v=1, J=8, \Omega=0, -$	65
8	10.0	$C^{12}O^{18}$	$v=1, J=6, \Omega=1, - \rightarrow v=1, J=8, \Omega=0, -$	52
9	12.2	$C^{12}O^{17}$	$v=0, J=6, \Omega=1, + \rightarrow v=0, J=8, \Omega=0, +$	42
10	16.040	$C^{12}O^{16}$	$v=0, J=6, \Omega=1, - \rightarrow v=0, J=4, \Omega=2, -$	31
11	16.1	$C^{12}O^{17}$	$v=1, J=6, \Omega=1, + \rightarrow v=1, J=8, \Omega=0, +$	32
12	17.8	$C^{13}O^{17}$	$v=0, J=6, \Omega=1, - \rightarrow v=0, J=8, \Omega=0, -$	30
13	19.253	$C^{12}O^{16}$	$v=0, J=6, \Omega=1, + \rightarrow v=0, J=4, \Omega=2, +$	26
14	19.470	$C^{12}O^{16}$	$v=0, J=6, \Omega=1, - \rightarrow v=0, J=8, \Omega=0, -$	−26
15	19.917	$C^{12}O^{16}$	$v=1, J=6, \Omega=1, - \rightarrow v=1, J=4, \Omega=2, -$	25

$^{12}C^{16}O$ at 1.648 GHz and 2.459 GHz (#1 and #3 of Table 1). When μ changes, the frequencies of these two transitions will change in opposite directions, *i.e.*, when μ becomes larger, the transition frequency in the $v=0$ will decrease while the transition frequency in the $v=1$ will increase. Combined these two transitions have a sensitivity which is 500 times larger than an ordinary rotational transition. It is instructive to compare the sensitivity to what one would expect in a pure Hund's case (a). For the transition at 1.648 GHz we expect a sensitivity of $-A/\nu = -41.45 \times 29.979/1.648 = -754$ which is 2.5 times larger than calculated using the model that includes the coupling between the different Ω-ladders. This is a warning that neglecting relevant couplings leads to an overestimation of the sensitivity.

Transitions between levels of different Ω-ladders are sensitive to variations of both μ and α. As the spin orbit energy scales as α^2,[12,13] in a pure Hund's case (a) the sensitivity of the 2-photon transitions to a variation of α is given by 2 A/ν. Mixing between different Ω-ladders will decrease the sensitivity to a variation of α. To first order, K_α will decrease in the same way as K_μ, hence, for the different transitions listed in Table 1, K_α is estimated to be two times larger than K_μ.

A proposed experiment in metastable CO

In this section we will present a molecular beam machine that is currently under construction at the Laser Centre Vrije Universiteit to measure 2-photon microwave transitions in metastable CO, and estimate the accuracy that may be achieved. We will focus on the $J=6$, $\Omega=1$, + $\rightarrow$ $J=8$, $\Omega=0$, + transitions in the $v=0$ and $v=1$ of $^{12}C^{16}O$ at 1.648 GHz and the 2.459 GHz, respectively, as these offer the highest sensitivity and are located in a convenient frequency range. Furthermore, $C^{12}O^{16}$ is the most abundant isotope (99%) and both C^{12} and O^{16} have a nuclear spin equal to zero. As both transitions differ only in vibrational energy (and sensitivity coefficient), systematic shifts due to stray magnetic or electric fields will be similar, and hence will cancel to first order. The other transitions listed in Table 1, as well as Λ-doublet transitions that are located in the same frequency range might be used to check for various systematic errors.

As mentioned, astronomical observations suggest that $\Delta\mu/\mu$ might change by 2×10^{-15} yr^{-1}. [5] The most stringent laboratory test of μ-variation is set by comparing vibrational transitions in SF_6 with a caesium fountain over 2 years, which has

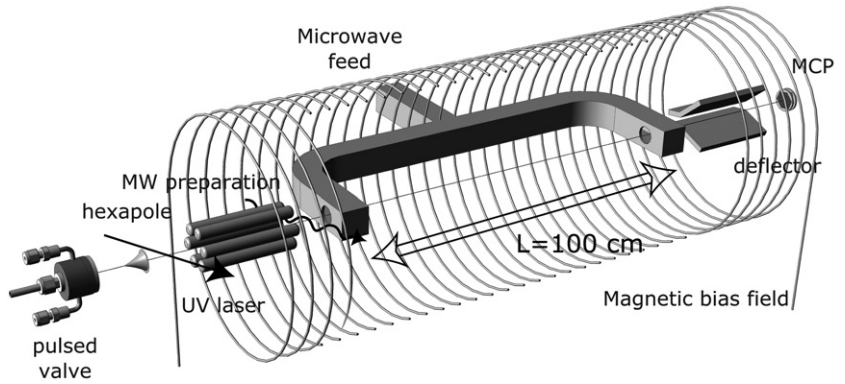

Fig. 4 Schematic view of a molecular beam apparatus to measure 2-photon microwave transitions in metastable CO.

resulted in a limit for the variation of $\Delta\mu/\mu < 5.6 \times 10^{-14}$ yr^{-1}. [7] In order to achieve a sensitivity in the order of 10^{-15} yr^{-1} the 2-photon transitions should be measured with a fractional accuracy of 10^{-12}. Although demanding, this seems possible.

Fig. 4 shows a schematic of a molecular beam apparatus that will be used to measure 2-photon microwave transitions in metastable CO. The machine is largely similar to the familiar magnetically deflected cesium beam clock[27]—clocks that have routinely reached fractional accuracies below 10^{-13}—the main difference being that the inhomogeneous magnetic fields are replaced by inhomogeneous electric fields. Due to its large vapor pressure and small polarisability, it is straightforward to produce an intense beam of CO molecules. Using pulsed laser light around 206 or 199 nm, the spin forbidden $a^3\Pi_1(v = 0, J = 6, -) \leftarrow X^1\Sigma^+(J = 6)$ or $a^3\Pi_1(v = 1, J = 6, -) \leftarrow X^1\Sigma^+(J = 6)$ is driven. These states are the upper components of the $J = 6$, $\Omega = 1$ state and have a positive Stark shift. Hence molecules in these states can be focused into the microwave cavity using either a quadrupole or hexapole or a combination of the two. Before the molecules enter the cavity they are driven to the lower component of the $J = 6$, $\Omega = 1$ state by inducing the Λ-doubling transition using pulsed microwave radiation around 6.5 GHz.

The 2-photon transition is measured using Ramsey's separated oscillatory fields method.[28] In the first cavity a coherent superposition of the lower component of the $J = 6$, $\Omega = 1$ and $J = 8$, $\Omega = 0$ state is created. During free flight between the two cavities, the phase of this coherent superposition will evolve. If there is no phase difference between the wavefunction and the microwave field—the microwave field is exactly at resonance—all molecules will be driven to the $J = 8$, $\Omega = 0$ state. If there is a π difference between the phase of the microwave field and the wavefunction, molecules will be driven to $J = 6$, $\Omega = 1$ state. Thus, if the frequency of the microwave field is scanned, an interference pattern is observed. The width of the fringes is determined by the time it takes for the molecules to pass the distance between the two cavities. If the distance between the cavities is taken to be a meter and the molecules have a velocity of about 500 m s^{-1}, the fringes will have a width of about 250 Hz. A homogeneous magnetic field is applied throughout the beam tube, to shift all resonances out of resonance, except for the $M = 0 \rightarrow M = 0$. Note that, as this magnetic field is perpendicular to the electric field, the magnetic field does not influence the pre and post state-selection. After the microwave cavity the molecules pass an inhomogeneous electric field that will deflect molecules in the $J = 6$, $\Omega = 1$ state while it will not influence the trajectories of molecules in the $J = 8$, $\Omega = 0$ state. Metastable CO molecules are detected by letting them impinge onto a multichannel plate (MCP) detector. The 6 eV internal energy of the metastable CO molecules is sufficient to free electrons at the surface of the MCP detector. These electrons are

multiplied and accelerated towards a phosphor screen. Subsequently, a digital camera is used to record the image on the phosphor screen.[29] The possibility to record the number of molecules in the $J = 6$, $\Omega = 1$ and $J = 8$, $\Omega = 0$ state *simultaneously* makes it possible to normalize the beam on a shot to shot basis which increases the signal to noise ratio. Note that any molecules remaining in the upper component of the $J = 6$, $\Omega = 1$ will be deflected in the opposite direction to molecules in the lower component and hence will not cause any background signal.

A frequency measurement is characterized by its statistical uncertainty and its accuracy—how well the measured frequency agrees with the unperturbed molecular frequency. A measure of the statistical instability as a function of measurement time is provided by the Allen variance,[27]

$$\sigma_y(\tau) = \frac{1}{Q}\frac{1}{\sqrt{N\tau/\tau_c}}$$

where Q is the quality factor of the transition given by the transition frequency over the measured linewidth, $\nu/\Delta\nu$, N is the number of metastable molecules detected per cycle, τ is the measurement time and τ_c is the duration of a single cycle. As mentioned, if we assume that the two cavities are separated by a distance of 1 m, and the velocity of the beam is on the order of 500 m s^{-1}, the interaction time is 2 milliseconds and the measured linewidth will be about 250 Hz. This corresponds to a Q-factor of 1×10^7. We estimate that it should be possible to detect 1000 or more molecules per cycle. At a repetition frequency of 10 Hz, we find $\sigma_y = 1 \times 10^{-9}\ \tau^{-1/2}$. This implies that a measurement time of about 1 h is required to reach an accuracy of 2×10^{-11}, and 300 h to reach an accuracy of 1×10^{-12}.

Ultimately, the precision will be limited by systematic shifts. With a careful design it should be feasible to keep errors due to the second order Zeeman and Stark shifts and blackbody radiation below 10^{-12}. Note that in caesium fountain clocks[10] these systematic effects are compensated at the level of 10^{-16}. Moreover, as the two transitions that will be compared differ only in vibration, we expect that most systematic errors will—to a very large extent—cancel. An open question is if the high power, necessary to induce the 2-photon transitions, leads to unacceptably large light shifts. Again, the shifts in both transitions are expected to be similar and they will partly cancel.

Other molecules

The precision that will be obtained on measuring the proposed 2-photon transitions in metastable CO will be limited by the lifetime of the metastable CO, which is on the order of 3 milliseconds for the $J = 6$, $\Omega = 1$ and $J = 8$, $\Omega = 0$ state. In this section we will discuss a number of other molecules where a cancellation of the fine structure and rotational interval might be expected to occur. We are particularly interested in molecules that can be decelerated using time-varying electric fields, such that the transition can be measured in a slow molecular beam[17,30] or in a molecular fountain.[18] In Bethlem *et al.*[31] a list of candidate molecules for Stark deceleration was presented. Most molecules on that list have by now indeed been decelerated. If we discard all polyatomic molecules—which are interesting in their own right—we are left with CH, CF, CO ($a^3\Pi$), LiH, NH ($a^1\Delta$), NO, OH, OD, SH. In what follows, we will discuss the suitability of these molecules to detect μ-variation using near degenerate rotational levels in different Ω-manifolds.

CH

The ground state of CH is $^2\Pi$. The spin orbit constant and rotational constant are $A = 27.95$ cm^{-1} and $B = 14.457$ cm^{-1}, respectively.[32] Due to the small ratio of A to B

the molecule is best described by a Hund's case (b) coupling scheme even for low J, and no degeneracies will occur. For CD, the spin orbit constant and rotational constant are $A = 27.95\ \mathrm{cm}^{-1}$, and $B = 7.8\ \mathrm{cm}^{-1}$. Although the ratio of A to B is increased by a factor of 2 compared to CH, CD is still very much case (b) even in the lowest J.

CF

The ground state of CF is $^2\Pi$. The spin orbit constant and rotational constant are $A = 77.12\ \mathrm{cm}^{-1}$ and $B = 1.417\ \mathrm{cm}^{-1}$, respectively.[32] Due to the large ratio of A to B, CF is well described by Hund's case (a). The two Ω-manifolds are expected to have a near-degeneracy at $J \approx 13$. More detailed calculations are needed to determine the frequency of the 2-photon transition and its sensitivity. However, the fact that the degeneracy occurs at high J, makes CF less suitable.

LiH

The ground state of LiH is $^1\Sigma$. As $\Lambda = 0$, it follows a Hund's case (b) coupling scheme.

NH

NH can be decelerated in the long lived $a^1\Delta$ state. This state is best described in Hund's case (b).

NO

The ground state of NO is $^2\Pi$. The spin orbit constant and rotational constant are $A = 123.26\ \mathrm{cm}^{-1}$ and $B = 1.672\ \mathrm{cm}^{-1}$, respectively.[32] Due to the large ratio of A to B, NO is well described by Hund's case (a). For $^{14}N^{16}O$ the two Ω-manifolds have near-degeneracies at $J = 18.5$ and $J = 19.5$. The smallest frequencies are around 70 GHz, which results in an enhancement of about 60. Smaller frequencies and correspondingly larger enhancement might be obtained with other isotopes of NO, however, the high J at which the degeneracy occurs is a disadvantage.

OH

The ground state of OH is $^2\Pi$. The spin orbit constant and rotational constant are $A = -139.21\ \mathrm{cm}^{-1}$ and $B = 84.881\ \mathrm{cm}^{-1}$, respectively.[32] Due to the negative A constant the $^2\Pi_{3/2}$ lies below the $^2\Pi_{1/2}$ state. If this would not have been the case, no near-degeneracies would have occurred due to the small A to B ratio. However, as a result of spin–orbit inversion, a near-degeneracy occurs between the $J = 7/2$, $\Omega = 3/2$ and $J = 3/2$, $\Omega = 1/2$ states with a 2-photon transition frequency of 220 GHz and an estimated enhancement to a μ-variation of about 10. The situation might be more favorable in OD.

SH

The ground state of SH is $^2\Pi$. The spin orbit constant and rotational constant are $A = -376.9\ \mathrm{cm}^{-1}$ and $B = 9.461\ \mathrm{cm}^{-1}$, respectively.[32] Due to the large ratio of A to B, SH is well described by Hund's case (a). The two Ω-manifolds are expected to have a near-degeneracy at $J \approx 12$. More detailed calculations are needed to determine the frequency of the 2-photon transition and its sensitivity.

Conclusions

In this paper we have shown that the sensitivity to a variation of the proton–electron mass ratio, μ, and the fine-structure constant, α, is enhanced due to near degeneracy

between rotational levels in the fine structure ladders of molecular radicals. This is an extension to the work of Flambaum[12] and Flambaum and Kozlov,[13] who showed that the relative sensitivity to a variation of μ and α is enhanced due to cancellation of hyperfine intervals with rotational intervals and cancellation of fine structure intervals with vibrational intervals. Whereas the cancellations discussed in ref. [12] and [13] occur in heavy molecules, the cancellations discussed in this paper occur in light molecules. As techniques to manipulate and cool molecules are more adapted to light molecules, a higher precision might be expected for these molecules.

We have presented a detailed calculation, including all relevant couplings, that show that a degeneracy occurs in the various natural isotopomers of carbon monoxide in its $a^3\Pi$ state. The most suitable transitions are the $J = 6$, $\Omega = 1$, + $\rightarrow$ $J = 8$, $\Omega = 0$, + transitions in the $v = 0$ and $v = 1$ of $^{12}C^{16}O$ at 1.648 GHz and the 2.459 GHz, respectively, which have a combined sensitivity to a μ-variation on the order of 500, and an estimated combined sensitivity to an α-variation of 1000. It seems possible to measure the 2-photon transitions with a fractional precision on the order of 10^{-12}, which would result in a limit for μ-variation on the order of 10^{-15} yr^{-1}.

The enhanced sensitivity due to the near-degenerate fine-structure levels should occur in many other light molecules as well. It is our hope to identify a molecule that has a suitable level structure and that can be cooled using one of the existing cooling techniques. We have performed a check for a number of seemingly promising molecules. But it turned out that these molecules all have either a too small A/B ratio—such that the molecule is no longer well described in a Hund's case (a) coupling scheme— or a too large A/B ratio—in which case the near degeneracy occurs at high J. We encourage the attendants of the Faraday meeting to come forward with suggestions for suitable molecules.

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